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THE COMPRESSIBILITY OF VITREOUS SILICA

Abstract

To explain the increase of compressibility of vitreous silica with pressure, it is assumed that there is a possibility of bending of the Si-O-Si lines in the structure. Calculations of network energies show that this is a reasonable assumption. Because of the randomness of the glass structure, it is not possible at this time to get more than a qualitative agreement between calculated and experimental values.

Introduction

Most ionic crystals show a compressibility which decreases with increasing pressure. This might be expected, since in the absence of external pressure, the size of the crystal lattice is such that the Coulomb forces between ions which, on the whole, act to pull the lattice together and reduce interionic distances are exactly balanced by the repulsive forces which have appreciable value only at very close distances and whose magnitude varies inversely as a very much higher power of the interionic spacing than the second power obeyed by the Coulomb forces. Under increasing pressure, as the ions are forced

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together, these repulsive forces increase very rapidly and it
becomes increasingly difficult to decrease the spacing. In
other words, the compressibility decreases.

Measurements by Bridgman[1] have shown that the compressibility
of silica glass increases with increasing pressure. This means
that it is unlikely that the deformation consists entirely of
a decrease of all interionic distances by the same ratio since
this would bring increasingly into play the high power repulsive
forces which would bring about a decrease in compressibility.
We must look, therefore, for some other mechanism. According
to the usual ideas on the structure of vitreous silica the
structure is rather open with numerous empty spaces. This
structure might allow a straight line, originally connecting
three adjacent ions, to bend under the action of pressure.
In particular, one might expect the line Si-O-Si which according
to Warren's X-ray work is or approaches a straight line to
bend slightly in the middle. It was in an attempt to find out
if this is a reasonable explanation that the following calcula-
tions were undertaken.

Explanation of Method

While there is good evidence for some degree of covalent
binding between silicon and oxygen, it was felt to be worth-

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[1] Robert B. Sosman, The Properties of Silica, The Chemical
Catalog Co., Inc., New York, 1927.

while to investigate the effect using a purely ionic model to find out if consideration of central forces only is sufficient to explain, at least qualitatively, the behavior of vitreous silica under compression.

As will be shown, within the limits of the assumptions made, it is possible to calculate the energy of the network by considering the distance between each ion and every other ion and the nature of the attraction or repulsion between each pair.

To find the equilibrium state at zero external pressure, we choose those values of the interionic spacings which make the energy a minimum. Under the action of external pressure, we assume some definite smaller volume and calculate the interionic spacings again to give the minimum energy for this compressed state. This new minimum will be greater than the energy for zero external pressure; from the relations between this new energy and its corresponding volume, it is possible, as will be shown, to calculate the pressure required to produce this state and hence to calculate the compressibility.

On the basis of these energy calculations alone, it is possible to decide, for each compressed state, whether minimum energy is achieved by maintaining the Si-O-Si lines as straight lines or by allowing them to bend.

Assumed Structure

On the basis of the generally accepted structure for vitreous silica, it was assumed that in the undisturbed state each Si ion is surrounded tetrahedrally by four O ions, and

that the line drawn from a Si ion to any one of its four
neighboring oxygens will, if produced, go through another
Si ion which is itself surrounded tetrahedrally by four
oxygens.

On deformation it is assumed that the network of Si
ions does not distort but merely reduces uniformly in linear
dimensions. The possibility is assumed that an oxygen ion,
originally lying at the exact midpoint of the line joining
two neighboring Si ions, moves out of line as the Si ions
start moving together.

Relationships Between Neighbors

For the purpose of the energy calculations it is necessary
ideally to know the distance between each ion and every other
ion. Since in a glassy structure, in contrast to a crystalline
structure, there is considerable randomness of structure beyond
the second or third nearest neighbor, it is probable that a
fairly good approximation of the energy arising from the Coulomb
interactions can be obtained by limiting attention to a fairly
close group of neighbors around each ion, so chosen that the
structure outside this group is electrically neutral.

In the undisturbed state the following neighbors will be
considered. Each Si ion has four oxygens at distance a and
four Si at distance b where b is equal to 2a. Further out
there will be twelve oxygens at a distance d where

$$d = \frac{\sqrt{57}}{3} a \qquad (1)$$

Of these we consider only six which means that the net charge on the neighbors is -4 which exactly balances the charge of plus 4 on the silicon and leaves a neutral mass surrounding these neighbors. The contribution of this neutral mass is assumed to be zero on the average.

Around each oxygen there are two closest silicon ions at a distance a and six oxygens at a distance c where

$$c = \frac{2\sqrt{6}}{3} a \qquad (2)$$

Of these silicons at distance d we count only 3/2 in order to maintain neutrality outside these neighbors. On distortion we do not assume that b is equal to 2a but do assume that on the average

$$c = \frac{2\sqrt{6}}{3} a \qquad (3)$$

This is equivalent to saying that after distortion each silicon is still surrounded tetrahedrally by four oxygens although the Si-O-Si lines are no longer straight.

The quantity d will now involve both a and b. On the average it will be assumed that d is given by

$$d^2 = a^2 + b^2 + \frac{2ab}{3} \qquad (4)$$

This averaging of distances to second nearest neighbors seems justified because of the randomness of a glassy structure as contrasted to the definite periodicity of a crystalline structure.

Energy

The energy of the lattice arising from the Coulomb interactions is

$$\frac{1}{2} \sum_n Z_n e \, \phi_n \tag{5}$$

where e is the magnitude of the charge on an electron, Z_n is the number of plus charges carried by ion n and ϕ_n is the potential at the location of ion n arising from all its neighbors. The 1/2 arises because in this summation every ion pair is considered twice.

The energy per SiO_2 molecule will therefore be

$$\frac{1}{2} \left\{ 4e \, \phi_{Si} + 2(-2e) \, \phi_o \right\} \tag{6}$$

where ϕ_{Si} is the average value of the potential at a silicon location. This may be written

$$2e(\phi_{Si} - \phi_o) \tag{7}$$

On the basis of our previous assumptions concerning neighbors

$$\phi_{Si} = -4 \, \frac{2e}{a} + 4 \, \frac{4e}{b} - 6 \, \frac{2e}{d}$$

$$= e(\frac{8}{a} + \frac{16}{b} - \frac{12}{d})$$

$$\phi_o = 2 \, \frac{4e}{a} - 6 \, \frac{2e}{c} + \frac{3}{2} \, \frac{4e}{d}$$

$$= e(\frac{8}{a} - \frac{12}{c} + \frac{6}{d}) \tag{8}$$

This gives for the energy per SiO_2 molecule

$$2e^2 \, (\frac{16}{a} + \frac{16}{b} + \frac{12}{c} - \frac{18}{d})$$

$$\text{or} \quad e^2 \, (\frac{-32}{a} + \frac{32}{b} + \frac{24}{c} - \frac{36}{d}) \tag{9}$$

Contribution of Repulsive Terms

The above magnitude becomes increasingly negative as the network shrinks in size. A minimum value for the energy is possible because of the repulsion between ions which arises at small distances of separation and whose magnitude is frequently approximated by an expression of the type

$$\frac{A}{r^n} \tag{10}$$

where n may be in the neighborhood of 10. Since this falls off so rapidly with distance, not too much error is introduced in considering interactions only between nearest neighbors. In this case the energy per molecule arising from this source is of the form

$$\frac{e^2 B}{a^{n-1}} \tag{11}$$

where B is a constant and a is the silicon-oxygen distance. The factor e^2 is included in the constant merely for convenience in combing this repulsive energy with the Coulomb energy given in equation (9). The repulsive energy (11) added to the Coulomb energy (9) has a minimum value for some value of a which is the zero pressure equilibrium value of a.

Relations Between Energy and Pressure

As shown, for instance, in Chapter II of Seitz' Modern Theory of Solids[2] the relation between the pressure, energy and volume of a solid is

$$p = -\frac{\partial E}{\partial V}$$

[2] Frederick Seitz, The Modern Theory of Solids, McGraw-Hill Book Co., New York, 1940

Under zero pressure the solid reaches a state of minimum energy where

$$\frac{E}{V} = 0$$

The connection between energy and volume as deduced from our previous calculation enables us to assign a pressure to each volume state of the glass.

To compute the compressibility in any state we use the relation

$$\frac{\partial^2 E}{\partial V^2} = \frac{1}{V \beta}$$

where β is the compressibility. In this formula E is the energy per mole and V is the molar volume. The connection between V and the quantity b we have been using is obtained by using the fact that V is proportional to the cube of b and the fact that we know from experiment the molar volume of vitreous silica in the unstressed state.

Factors Determining the Form of Network

In the following calculations it will be assumed that as the network is compressed there is no distortion of the part of the network which consists only of Si ions but merely a shrinkage. There is allowance, however, for a bending of the Si-O-Si lines and this is handled as follows.

A value of the quantity b is assumed which is the closest Si-Si spacing. Values of B and n for the constants in the repulsion energy term are also assumed. Then for each value of b a series of values of a is taken whose smallest value is $\frac{b}{2}$

and the energy of the network is computed. That value of a
which makes the energy a minimum for the value of b chosen is
taken as the correct one. Thus, the bending or non-bending
of the Si-O-Si lines (b less than 2a or b equals 2a) is merely
a matter of what configuration gives the lowest energy for the
value of b selected.

Results

As a start it was assumed that the Si-Si spacing in the
unstressed state is 3.24 A. For want of any very good informa-
tion the assumption was made that silicon and oxygen ions repel
each other according to an inverse eleventh power law or that
the energy arising from this effect varies as the inverse tenth
power of the separation.

First it was assumed that B has that value which makes
the energy a minimum for a silicon-silicon distance of 3.24 A.
When this value was used, it was found that for the entire
range of compressions covered in Bridgman's work, the energy
relations required that the oxygens lie along the silicon-
silicon line. This, as would be expected, gave a compressibility
which slowly decreased with increasing pressure. The Si-O-Si
lines did not bend until the volume decreased considerably
greater than that actually investigated. In units such that

$$\frac{e^2 B}{a^{10}}$$

has the dimensions of ergs per SiO_2 molecule this value of B is
about 120.

The explanation of this is very probably that, because of
the somewhat random manner in which vitreous silica or any glass

is put together, the Si-O-Si lines are not straight to begin
with as they would be in the high cristobalite structure but
are already slightly bent and ready to bend more immediately
when pressure is applied. This means that the unstressed
state does not correspond to a minimum energy state <u>within the
framework of the simple assumptions made</u>. The effect of the
random structure of the glass is, in fact, almost as if the
ideal structure, at first assumed, were subjected even at zero
pressure to a pressure sufficient to bend the Si-O-Si lines
slightly.

The network was then treated as if, at the equilibrium
spacing of 3.24 A, it were under such a pressure that, on
increasing the pressure, the Si-O-Si lines would start bending
within the range covered by the experiments.

A value of 160 for B required that even at a Si-Si spacing
of 3.24 A the Si-O-Si lines were already bent. A value of
1b meant that the Si-O-Si lines remained straight on compression
until the Si-Si distance was reduced from 3.24 A to 3.224 A;
on further compression, minimum energy was achieved by displacing
the oxygen ion from this line but keeping it in the plane which
perpendicularly bisected the line.

From 3.24 until the line starts to bend, there is a
slight decrease in compressibility. At the onset of bending
there is a sudden discontinuous change in compressibility
to a considerably higher value which on further compression
slowly starts to decrease. The suddenness of the increase
in compressibility is not in agreement with experiment. The
gradualness actually found is again probably caused by

the randomness of the vitreous structure. This randomness
probably results in a different degree of bending of the
various Si-O-Si lines throughout the structure. Increase
in compressibility arises only when the lines start bending.
It would then seem reasonable to assume that in the normal
state some of these lines are straight and some slightly bent.
Increase in pressure increases the number actually bent, and
this gradual onset of bending gives rise to the slow rather
than sudden increase in compressibility.

Conclusions

Since compressibility of vitreous silica starts to
increase immediately on increase of pressure, the calculations
would indicate that under zero or atmospheric pressure
there is already some bending of the Si-O-Si lines.

Because the increase in compressibility is gradual
rather than sudden, it might be concluded that there is
some randomness in the degree of bending of the Si-O-Si lines.

These conclusions are based on calculations using a
purely ionic model, and no attempt has been made to estimate
what the effect of some degree of covalency in the Si-O
binding might be.

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